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COMPETITIVE FORMATION OF PERACETYLATED α-L-ARABINOPYRANOSIDES AND β-L-ARABINOPYRANOSE 1,2-(ALKYL ORTHOACETATES) IN KOENIGS–KNORR CONDENSATIONS

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ABSTRACT

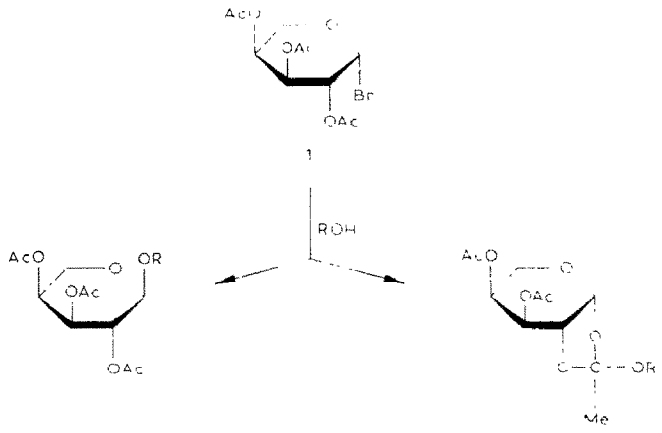
Mixtures of peracetylated β-L-arabinopyranose 1,2-(alkyl orthoacetates) and the corresponding α-L-arabinopyranosides, in ratios as high as 1:1.3, have been obtained from primary, secondary, and tertiary alcohols and 2,3,4-tri-*O*-acetyl-β-L-arabinosyl bromide, by reaction in dichloromethane–diethyl ether (3:1) in the presence of silver oxide and anhydrous calcium sulfate. Orthoester formation decreased when dichloromethane was replaced by the less-polar chloroform or carbon tetrachloride, and also when diethyl ether was replaced by the more bulky dibutyl or di-isopropyl ethers. The product distribution, which is unusual for Koenigs–Knorr condensations involving 1,2-*cis* acylglycosyl halides in the presence of silver oxide, may be ascribed to competitive inhibition of glycoside formation by complexation of the intermediate glycosyl cation with ether and to solvent polarity effects.

INTRODUCTION

Koenigs–Knorr condensation of alcohols and 1,2-*cis* acylglycosyl halides, in some cases, has produced 1,2-*cis* orthoesters instead of, or in addition to, the usual 1,2-*trans* glycosides[1]. This has been achieved by using such special solvent–catalyst systems as nitromethane–collidine[2], ethyl acetate–lead carbonate[3], or tetrahydrofuran and, mainly, organic silver salts, which were left to react with the glycosyl halide before the alcohol was added[4–7]. Most of this published work has been restricted to the *gluco* series. We now report that mixtures of peracetylated 1,2-*cis* orthoacetates and 1,2-*trans* glycopyranosides may also be formed from the respective 1,2-*cis* arabinopyranosyl bromide and a variety of alcohols, using standard Koenigs–Knorr catalyst and solvents, namely, silver oxide and dichloromethane–diethyl ether.

RESULTS AND DISCUSSION

When a solution of 2,3,4-tri-*O*-acetyl-β-L-arabinopyranosyl bromide (**1**) in dichloromethane was added slowly to an ethereal solution of 2-phenylethanol con-



2	R = PhCH	12
3	R = *p*-NO$_2$C$_6$H$_4$CH	13
4	R = PhCH$_2$CH$_2$	14
5	R = PhCH=CHCH	15
6	R = Me	16
7	R = Et	17
8	R = Pr	18
9	R = Me$_2$CH	19
10	R = R,S-Me$_2$C(OMe)H	20
11	R = Me$_3$C	21
22	R = H	23

taining silver oxide and anhydrous calcium sulfate, the arabinopyranoside **4** and the orthoester **14** were formed in the ratio of ~7:1.

When the reaction was repeated, using dichloromethane–diethyl ether (3:1) as the solvent for both **1** and 2-phenylethanol, nearly equal amounts of **4** and **14** were isolated (Table I), and t.l.c. indicated that the product ratio was approximately constant from the beginning of the reaction. With this solvent system, mixtures of the peracetylated orthoesters **12–21** and the arabinopyranosides **2–11** were also formed from **1** and nine primary, secondary, and tertiary alcohols. The differences in component ratios (Table I) should not be over-interpreted, as the two products are difficult to separate, and decomposition of the orthoester during the isolation procedure cannot be completely avoided. Apparently, aralkyl alcohols tend to yield slightly more, and bulky aliphatic alcohols considerably less, than the average amount of orthoester. These usually appeared as ~2:1 mixtures of their *exo* and *endo* isomers, except for **20**, which was mostly *exo*.

The sample of **1** used in the above reactions was not contaminated by the α-L anomer (which would normally yield orthoesters), as evidenced by m.p., specific rotation, and n.m.r. data, and did not mutarotate in dichloromethane–diethyl ether

TABLE I

RATIOS OF PERACETYLATED β-L-ARABINOPYRANOSE 1,2-ORTHOACETATES AND α-L-ARABINOPYRANOSIDES FORMED BY CONDENSATION OF **1** WITH ALCOHOLS IN DICHLOROMETHANE–ETHER (3:1)

Orthoester	*Glycoside*	*Total yield*[a] (%) *(orthoester + glycoside)*	*Ratio of orthoester to glycoside*
12	**2**	78	1:1.3
13	**3**	38[b]	1:1.4
14	**4**	74	1:1.3
15	**5**	62	1:1.9
16	**6**	88	1:2.6
17	**7**	74	1:3.6
18	**8**	67	1:2.9
19	**9**	64	1:2.3
20	**10**	37[c]	1:4.8
21	**11**	28[d]	1:13.0

[a]Based on **1**. [b]By-products: **22**, 32%; **24**, 6%; **25** obscured by unreacted *p*-nitrophenylmethanol. [c]By-products: **22**, 43%; **24**, 3%; **25**, 4%. [d]By-products: **22**, 45%; **24**, 8%; **25**, 7%.

TABLE II

SOLVENT INFLUENCE ON THE FORMATION OF **14** AND **4** IN CONDENSATIONS OF **1** WITH 2-PHENYLETHANOL

Solvent (volume ratio)	*Yield (%) of* **14** + **4**	*Ratio of* **14**:**4**
Dichloromethane–ether (75:25)	74	1:1.3
Dichloromethane–chloroform–ether (50:25:25)	77	1:2.0
Dichloromethane–chloroform–ether (25:50:25)	71	1:8.8
Chloroform–ether (75:25)	60	n.o.[c]
Chloroform–ether (49:51)[a]	n.d.[b]	n.o.[c]
Carbon tetrachloride–ether (75:25)	64	n.o.[c]
Dichloromethane–di-isopropyl ether (75:25)	76	1:3.7
Dichloromethane–dibutyl ether (75:25)	73	1:6.9

[a]Chloroform–ether mixture having maximal dielectric constant[8], *i.e.*, 6.0 at 20°. [b]Not determined. [c]No orthoesters detected.

Compounds **2**–**21** were characterised by elemental analysis (Table III), and by ^{13}C- and ^{1}H-n.m.r. spectroscopy (Tables IV and V).

Syntheses of orthoesters from 1,2-*cis* acylglycosyl halides[1-7] often involve the use of nucleophilic solvents as one of the critical conditions. However, only minute amounts of **14** were formed when **1** and 2-phenylethanol were condensed in diethyl ether or in dichloromethane. In dichloromethane–diethyl ether mixtures, on the other hand, the **14**:**4** ratio increased with increase in the concentration of ether, to reach a maximum at ~25% per volume (17 mol %), and then decreased (Fig. 1).

TABLE III

DATA FOR THE PERACETYLATED α-L-ARABINOPYRANOSIDES (**2**–**11**) AND β-L-ARABINOPYRANOSE 1,2-ORTHOACETATES[a] (**12**–**21**)

Compound	$[\alpha]_D$[b] *(degrees)*	*Molecular formula*	*Calculated (%)*		*Found (%)*	
			C	*H*	*C*	*H*
2	−20 (*c* 5)[c]	$C_{18}H_{22}O_8$	59.01	6.05	59.28	6.05
12	—				59.21	6.00
3	−11 (*c* 5)	$C_{18}H_{21}NO_{10}$	52.56	5.15[d]	52.69	5.24[e]
13	—				52.48	5.22
4	−8 (*c* 0.7)	$C_{19}H_{24}O_8$	59.99	6.36	59.74	6.26
14	—				59.96	6.34
5	−21 (*c* 6)	$C_{20}H_{26}O_8$	60.90	6.64	60.76	6.48
15	—				60.61	6.39
6	−11 (*c* 2)[c]	$C_{12}H_{18}O_8$	49.65	6.25	49.89	6.25
16[f]	—				49.40	6.12
7	−19 (*c* 5)[g]	$C_{13}H_{20}O_8$	51.31	6.63	51.57	6.36
17	—				51.08	6.47
8	−18 (*c* 6)	$C_{14}H_{22}O_8$	52.83	6.97	52.55	6.92
18	—				52.56	7.00
9	−10 (*c* 4)	$C_{14}H_{22}O_8$	52.83	6.97	52.57	6.83
19	—				53.03	6.78
10[h]	−1 (*c* 3)	$C_{17}H_{28}O_8$	56.66	7.83	56.38	7.83
20	—				56.77	7.74
11[h]	−26 (*c* 2)	$C_{15}H_{24}O_8$	54.21	7.28	54.06	7.04
21	—				n.d.[i]	n.d.[i]

[a] *exo,endo* Mixtures variable in isomer composition and optical rotation. [b] In chloroform solution. [c] Lit.[26] −24.4°. [d] Calc.: N, 3.40. Found: N, 3.38. [e] Lit.[27] D-enantiomorph, −11.9°. [f] Described by Kochetkov *et al.*[28]. [g] Lit.[29] −7°. [h] M.p.: **10**, 120–121°; **11**, 111°; all other compounds were syrups. [i] Not determined; quantities obtained did not permit microanalysis.

The same kind of solvent dependence of orthoester formation was observed with 3-phenylpropan-1-ol and *p*-nitrophenylmethanol. These results suggest that interaction of solvent with **1** determines the ratio of products.

Mixtures of an ether and a partially halogenated alkane may be more polar than either component[8], owing to the formation of hydrogen-bonded complexes[9]. Thus, although the dielectric constant of dichloromethane[8] (D = 8.93) is about twice that of diethyl ether[8] (D = 4.34), it should increase even further on combining these solvents in certain ratios. It was therefore suspected that orthoester formation in dichloromethane–diethyl ether mixtures was due, at least partially, to this increase in solvent polarity. To verify this, the diethyl ether content of the solvent was kept constant, and the dichloromethane was gradually replaced by chloroform, which forms less-polar ether complexes[8] (D_{max} = 6.00), or by carbon tetrachloride (D = 2.24) which does not form a complex[8]. As expected, the **14**:**4** ratio decreased markedly (Table II).

Orthoester formation also decreased when diethyl ether was replaced by the

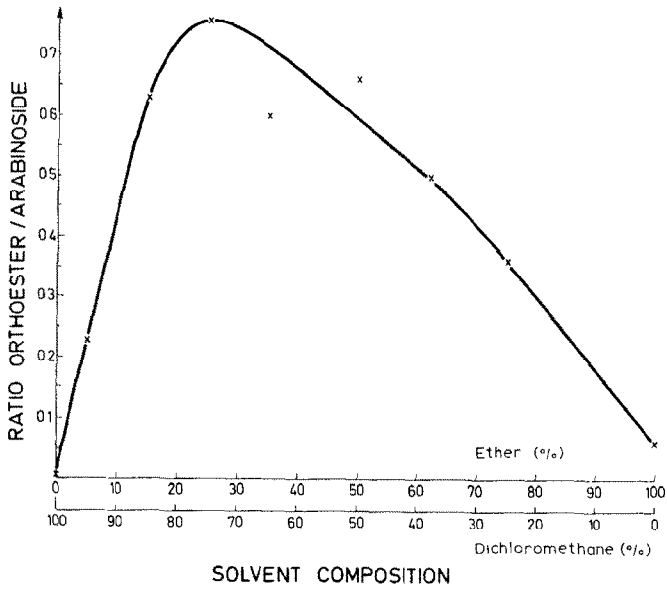
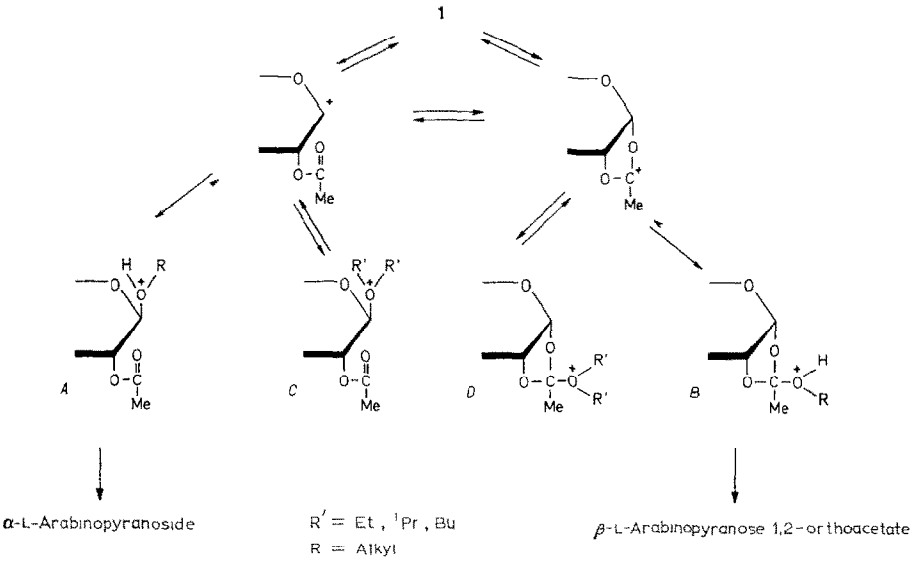


Fig. 1. Solvent dependence of **14**:**4** product ratios for the condensation of **1** and 2-phenylethanol. The figures are weight ratios determined after preparative t.l.c. of product mixtures. Total yields (**14** + **4**) were 58–74%.



Scheme 1. Proposed mechanism for the competitive formation of peracetylated α-L-arabinopyranosides and β-L-arabinopyranose 1,2-orthoacetates in ether-containing solvents.

TABLE IV

PARTIAL ^{13}C-N.M.R. DATA FOR ARABINOSIDES **2–11** AND ORTHOESTERS **12–21**

Arabinosides					*Orthoesters*						
Compound	*Chemical shifts (p.p.m.)*				*Compound*	*Chemical shifts (p.p.m.)*					
	AcO-2,3,4[a]					*AcO-3,4*		*Ethylidene*		*Sugar*	
	C=O	*CH_3*	*C-1*	*C-5*		*C-O (2C) singlet*	*CH_3 (2C) singlet*	*C-1*	*C-2*	*C-1*	*C-5*
	170.11	20.86									
2	169.97	20.71	99.51	62.91	**12**	*exo* 169.68	20.76	122.85	24.22	97.22	62.37
	169.29	20 61				*endo* 169.68	20.76	123.41	24.00	96.17	63.08
	170.07	20.81									
3	169.87	20.71	100.14	63.06	**13**	*exo* 169.72	20 76	123.05	24.51	97.27	62.47
	169.33	20.61				*endo* 169.72	20.76	123.56	24.02	95.90	63 35
	170.17	20.86									
4	169.97	20.61	100.87	63.15	**14**	*exo* 169.63	20.76	122.51	23.78	97.07	62.28
	169.24	20.61				*endo* 169.63	20.76	122.70	23.34	96.97	62.57
	170.17	20.86									
5	169.97	20.76	100.87	63.01	**15**	*exo* 169.76	20.78	122.85	24.17	97.17	62.33
	169.24	20.61				*endo* 169.76	20.78	123.09	23.73	96.58	62.96

	170.17	20.86									
6[b]	169.97	20.76	101.85	63.15	**16**	*exo* 169.72	20.76	123.04	23.78	97.22	62.38
	169.33	20.61				*endo* 169.72	20.76	123.29	23.24	96.53	63.01
	170.21	20.91									
7	170.07	20.76	100.77	63.20	**17**	*exo* 169.72	20.76	122.75	24.17	97.12	62.33
	169.33	20.66				*endo* 169.72	20.76	122.90	23.73	96.58	62.91
	170.11	20.86									
8	169.97	20.71	100.92	63.06	**18**	*exo* 169.72	20.76	122.70	24.07	97.17	62.28
	169.24	20.61				*endo* 169.72	20.76	123.00	23.68	96.68	62.96
	170.17	21.83									
9	169.92	20.86	99.75	63.20	**19**	*exo* 169.78	20.81	122.85	24.51	97.07	62.33
	169.14	20.61				*endo* 169.78	20.81	123.53	23.63	96.00	63.20
	170.26	20.90									
10a[c]	170.01	20.82	102.92	63.11	**20a**[c]	*exo* 169.81	20.84	123.53	25.70	97.07	62.30
	169.19	20.63				*endo* —	—	—	—	—	—
	170.15	20.93									
10b[c]	169.96	20.78	97.51	62.00	**20b**[c]	*exo* 169.81	20.84	123.53	25.39	96.84	62.30
	169.19	20.69				*endo* —	—	—	—	—	—
	170.31	20.91									
11	170.07	20.76	95.90	63.40	**21**	*exo* 169.78	20.81	122.75	24.12	97.17	62.38
	169.14	20.66				*endo* 169.78	20.81	n.d.[d]	23.6	96.63	62.90

[a]Values for three individual C=O and CH_3 groups. Carbonyl and methyl resonances appearing on the same line do not necessarily belong to the same acetyl group. [b]Lit.[20] 170.0, 169.4 (C=O); 20.8 (acetyl CH_3); 102.0 (C-1); 63.2 (C-5). [c]Two diastereomeric (*R* and *S*) arabinosides and orthoesters. [d]Not determined.

TABLE V

^{1}H-N.M.R. DATA FOR THE SUGAR PROTONS OF ARABINOSIDES **2–11** AND ORTHOESTERS **12–21**

Solvent	*Arabinosides*										*Orthoesters*[a]										
	Compound	*Chemical shifts (p.p.m., J in Hz)*						*Acetyl groups*			*Compound*		*Chemical shifts (p.p.m., J in Hz)*						*Acetyl groups*		*Ethylidene Me*
		H-1 ($J_{1,2}$)	*H-2* ($J_{2,3}$)	*H-3* ($J_{3,4}$)	*H-4* ($J_{4,5a}$)	*H-5a* ($J_{5a,5b}$)	*H-5b* ($J_{4,5b}$)						*H-1* ($J_{1,2}$)	*H-2* ($J_{2,3}$)	*H-3* ($J_{3,4}$)	*H-4* ($J_{4,5a}$)	*H-5a* ($J_{5a,5b}$)	*H-5b* ($J_{4,5b}$)			
$CDCl_3$	**2**	4.49	5.27	5.02	5.26	4.06	3.62	2.13	2.03	2.01	**12**	*exo*	5.60	4.35	5.35	5.25[c]	4.07	3.75	2.11	2.07	1.77
		(6.5)	(9.1)	(3.2)	(3.4)	(12.9)	(1.8)					*endo*	5.43	4.22	5.43	5.3	4.08	3.77	2.12	2.09	1.64
C_6D_6												*exo*	5.44	4.28	5.51	5.35	3.70	3.43	1.68	1.62	1.78
													(4.0)	(5.3)	(3.3)	(4.6)	(12.5)	(4.6)			
												endo	5.18	4.06	5.67	5.36	3.65	3.37	1.67	1.60	1.54
													(4.1)	(5.6)	(3.1)	(4.4)	(12.5)	(4.4)			
$CDCl_3$	**3**	4.57	5.31	5.07	5.30	4.08	3.67	2.15	2.09	2.05	**13**	*exo*	5.61	4.34	5.41	5.24[c]	4.07	3.76	2.12	2.08	1.79
		(6.5)	(9.1)	(3.5)	(3.5)	(12.9)	(1.8)					*endo*	5.40	4.22	5.38	5.29	4.10	3.78	2.12	2.08	1.65
C_6D_6												*exo*	5.45	4.28	5.49	5.35	3.73	3.48	1.72	1.67	1.75
													(4.0)	(5.4)	(3.4)	(4.5)	(12.5)	(4.6)			
												endo	5.07	3.99	5.54	5.31	3.66	3.37	1.67	1.60	1.50
													(3.7)	(5.2)	(3.0)	(4.8)	(12.5)	(4.8)			
$CDCl_3$	**4**	4.39	5.20	4.99	5.25	4.02	3.60	2.14	2.01	1.92	**14**	*exo*	5.38	4.06	5.29	5.15[c]	4.01	3.7	2.10	2.06	1.68
		(6.7)	(9.4)	(3.4)	(3.1)	(13.0)	(1.7)					*endo*	5.42	4.15	5.35	5.20	3.70	3.64	2.09	2.07	1.56
C_6D_6		4.14	5.62	5.13	5.26	3.67	2.92	1.73	1.67	1.59		*exo*	5.32	4.11	5.46	5.31	3.68	3.41	1.67	1.61	1.71
		(7.0)	(9.4)	(3.3)	(3.2)	(13.0)	(1.7)						(4.1)	(5.2)	(3.4)	(4.6)	(12.5)	(4.6)			
												endo	5.23	4.06	5.64	5.31	3.49	3.34	1.69	1.63	1.48
													(4.4)	(5.9)	(3.3)	(3.8)	(12.6)	(4.0)			
$CDCl_3$	**5**	4.41	5.24	5.04	5.27	4.04	3.61	2.14	2.08	2.04	**15**	*exo*	5.54	4.25	5.4 –	5.2[c]	4.04	3.73	2.11	2.06	1.70
		(6.6)	(9.2)	(3.3)	(3.3)	(13.0)	(1.7)					*endo*	5.40	4.17	5.39	5.29	4.04	3.74	2.10	2.08	1.57
C_6D_6												*exo*	5.42	4.25	5.50	5.34	3.69	3.42	1.67	1.61	1.76
													(3.9)	(5.3)	(3.3)	(4.6)	(12.5)	(4.6)			
												endo	5.19	4.05	5.66	5.37	3.71	3.40	1.67	1.61	1.52
													(4.2)	(5.6)	(3.3)	(4.2)	(12.4)	(4.3)			
$CDCl_3$	**6**	4.34	5.20	5.03	5.27	4.05	3.63	2.14	2.07	2.02	**16**	*exo*	5.58	4.31	5.4	5.2[c]	4.05	3.74	2.12	2.08	1.69
		(6.3)	(9.3)	(3.4)	(3.2)	(12.9)	(1.7)					*endo*	5.42	4.18	5.4	5.2[c]	4.10	3.78	2.11	2.09	1.56

C_6D_6												*exo*	5.40 (3.9)	4 23 (5.3)	5.48 (3 2)	5.33 (4 5)	3 68 (12 4)	3.41 (4.6)	1.67	1.60	1.73
												endo	5 16 (4.2)	4.03 (5.6)	5.63 (3.2)	n.a [b] (4 2)	3.71 (12 5)	3.40 (4.4)	1.67	1.60	1.48
$CDCl_3$	**7**	4.42 (6.5)	5.21 (9.4)	5 02 (3.1)	5.26 (3.1)	4 04 (13.1)	3.62 (1.8)	2.14	2.07	2.03	**17**	*exo*	5.57	4 30	5.4 ——	5.2[c]	4.05	3.74	2.12	2.08	1.70
												endo	5.42	n.a [b]	5.4 ——	5 2[c]	n a.[b]	n.a [b]	2.11	2 09	1.58
C_6D_6												*exo*	5.43 (4.2)	4.26 (5.2)	5.50 (3 3)	5.34 (4 5)	3.70 (12.4)	3.43 (4.5)	1.68	1.62	1.76
												endo	5.19 (4.2)	4.05 (5 7)	5 67 (3.2)	5.40 (4.2)	3.75 (12.4)	3.41 (4.3)	1.67	1 60	1.51
$CDCl_3$	**8**	4.41 (6.4)	5.21 (9.2)	5.03 (3.3)	5.27 (3.3)	4.04 (13.1)	3.62 (1.9)	2.07	2 04	2.03	**18**	*exo*	5.72	4 30	5.4 ——	5.2[c]	4 05	3.74	2.12	2.11	1.69
												endo	—	—	—	—	—	—	—	—	—
C_6D_6												*exo*	5.47 (4 0)	4 30 (5 3)	5.51 (3.3)	5 35 (4.6)	3 71 (12.3)	3 44 (4.6)	1.68	1.62	1 76
												endo	5.20 (4.2)	4 07 (5 8)	5.67 (3 2)	5.41 (4.1)	3.76 (12.5)	3 41 (4.2)	1.67	1.60	1.52
$CDCl_3$	**9**	4.45 (6 5)	5.18 (9 0)	5.02 (3.1)	5.26 (3.0)	4.04 (13 1)	3.61 (1.7)	2.14	2.06	2.02	**19**	*exo*	5 57	4.30	5.3 ——	5.2[c]	4.05	3 73	2.12	2.08	1 70
												endo	—	—	—	—	—	—	—	—	—
C_6D_6												*exo*	5 45 (3 9)	4.33 (5.3)	5.48 (3.3)	5.36 (4.4)	3 71 (12.5)	3.42 (4.5)	1 67	1.62	1.75
												endo	5.10 (3.9)	4.01 (5.4)	5.63 (3.1)	5.44 (4 4)	3.74 (12 4)	3.40 (4 6)	1.66	1.61	1.51
C_6D_6	**10**[a]	4.26	5 55	5 21	5.33	3.75	3.01	1.74	1.73	1.58	**20**[a]	*exo*	5.45	4.39 4.36	5.84	5 36	3.68	3 41	1.65 1.63	1.60 1.61	1 78 1.77
		(6 6)	(9.0)	(3.4)	(3.3)	(13.0)	(1.6)						(3.9)	(5.3)	(3 1)	(4 5)	(12.5)	(4 4)			
		4.12 (7.2)	5.63 (9.7)	5.13 (3 4)	n.a.[b] (2.7)	3.69 (13.0)	2.96 (1.5)	1.78	n a.[b]	n.a.[b]											
$CDCl_3$	**11**	4.56 (6.3)	5.18 (9.4)	5.02 (2.9)	5.25 (2.4)	4.02 (13.2)	3 60 (1 5)	2 14	2.05	2.02	**21**	*exo*	- -	—	—	—	-	—	—	—	—
												endo	—	—	—	—	—	—	—	—	—
C_6D_6		4.35 (7.1)	5 57 (9.5)	5 14 (3 4)	5.25 (2.7)	3.67 (13.2)	2.88 (1 3)	1.74	1.57			*exo*	5 43 (4 1)	4.26 (5.3)	5 50 (3.3)	5.35 (4 6)	3 69 (12.3)	3.42 (4.6)	1.68	1 67	1.76
												endo	5 19 (4.2)	4.05 (5.6)	5.67 (3.5)	n.a.[b] (4.4)	3.75 (12.7)	3.41 (4.6)	1.65	1.60	1 51

[a]Two diastereomeric (*R* and *S*) arabinosides (**10**) and orthoesters (**20**), the latter with coincident signals for H-1,3,4,5 and aglycon-configuration-independent H,H-coupling constants. [b]Not assignable. [c]Complex 2-proton multiplet. [d]Coupling constants given for solutions in benzene, which afford better resolution. Coupling constants for solutions in chloroform, as far as discernible, were not significantly different.

equally polar and nucleophilic, but more bulky, di-isopropyl and dibutyl ethers (Table II). This indicates some specific effect of the ether on the course of the reactions.

The explanation for these results proposed in Scheme 1 is based on intermediates that have been proved[7-10] (*C*) or postulated[11] (*B*) to exist in related systems, or which were deduced by straightforward analogies (*A*,*D*). The free cations shown are assumed to be in solvent-dependent equilibria with the corresponding, intimate ion-pairs involving the bromide ion. The ambident sugar cation formed[12] by silver ion-catalysed dissociation of **1** is presented as an equilibrium mixture of the glycosyl cation and the acetoxonium ion. These equilibrate with ether complexes *C* and *D*, which are not subject to further transformations, and with alcohol complexes *A* and *B*, which are irreversibly deprotonated to give the α-L-arabinopyranoside and the β-L-arabinopyranose 1,2-orthoacetate, respectively.

Although the glycosyl cation is more reactive towards alcohols than is the acetoxonium ion, and thus α-L-arabinopyranosides are always the preponderant condensation products, there seem to be two ways of promoting orthoester formation in dichloromethane–diethyl ether mixtures. Firstly, the positive charge of the acetoxonium ion is more dispersed, the effective ion radius larger, and the resulting attraction of its counter anion smaller than for the glycosyl cation. Dichloromethane–diethyl ether mixtures should be sufficiently polar to promote dissociation of these, more loosely associated, ion pairs. The pool of free ions should then be relatively enriched in the acetoxonium ion and its derivatives *B* and *D*. As free ions are generally more accessible to reactants than those bound in ion pairs, the formation of orthoesters should be promoted.

Secondly, in an ether-containing solvent, and without an excess of the aglycon alcohol, a significant fraction of the sugar reactant should be in the form of ether complexes *C* and *D*. For the condensation to proceed, these complexes have to dissociate to the uncomplexed glycosyl and acetoxonium ions, which may then be captured by the alcohol. As *C* is stabilised by the reverse anomeric effect, its dissociation requires more energy than that of *D*. This should bring about partial competitive inhibition, by diethyl ether, of the glycoside pathway, causing the arabinosyl bromide also to react *via* the orthoester route.

The effect of competitive inhibitors can generally be reversed by an excess of the reactant. Indeed, increasing the concentration of 2-phenylethanol (~10-fold) reduced the relative yield of **14** (~15-fold).

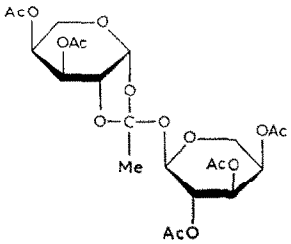
In summary, orthoester formation from 1,2-*cis* acylglycosyl halides may be interpreted as a backdoor mechanism operating when the glycosyl cation is competitively complexed by a non-reactive nucleophile, in a sufficiently polar solvent. This interpretation could also explain other results[2-7], as well as the partial inhibition by diethyl ether of orthoester formation from the 1,2-*trans* 2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl bromide (the complex corresponding to *C* (Scheme 1) is *destabilised* by the reverse anomeric effect)[13,14].

The reaction of **1** with hydroxy compounds other than alcohols, in dichloromethane–diethyl ether (3:1), was not studied systematically. However, some conclu-

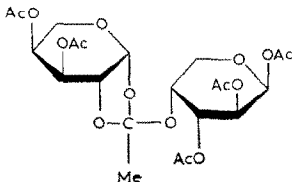
sions are possible from the structure of the by-products, which were obtained in all condensations with alcohols, and even preponderant with those of low reactivity.

The most prominent by-product was identified, by independent synthesis, as 2,3,4-tri-*O*-acetyl-L-arabinopyranose (**22**). Its formation did not require the presence of an alcohol; most probably it was formed by hydrolysis of **1** with the water adsorbed to silver oxide[15] even after extensive drying.

Each isolated sample of **22** showed an $\alpha\beta$-ratio of $\sim 3:7$. That this is not merely due to mutarotation during purification was indicated by two further by-products that generally accompanied **22**. They were identified, by analogy with observations in the *gluco*[11] and *manno*[15] series, as peracetylated β-L-arabinopyranose 1,2-ortho-acetates (**24** and **25**) containing either **22α** or **22β** as the alcohol moiety. It is probable that **24** and **25** are formed by the reaction[12] of **22** and **1**. Indeed, when **22αβ** reacted with **1** in dichloromethane–diethyl ether, orthoesters **24** and **25** were the main products. Of their glycosidic analogues, only the peracetylated α-L-arabinopyranosyl α-L-arabinopyranoside (**26**), formed in very small yield, was identified (tentatively).



24



25

These side-reactions may also be explained in terms of Scheme 1, assuming competition of several reactive nucleophiles; **22α** most probably arises *via A* (R = H), and also *via B* (R = H) and subsequent rearrangement of the resulting, unstable orthoacid **23**[13]. Concerning the formation of **22β**, water molecules may be small enough to attack *C*, or the glycosyl cation, from the axial side, whereas larger nucleophiles are hindered by the bulky AcO-2. Also, the orthoester–glycoside rearrangement, and hence the conversion **23**→**22α**, may not be stereospecific[16]. The preponderant orthoester (**24**,**25**) formation from **1** and **22**, as opposed to the preponderant glycoside formation from alcohols, may be due to the fact that **22** is a softer base than alkoxyl, and thus should attack preferentially the acetoxonium ion, which is a softer acid than the glycosyl cation.

EXPERIMENTAL

General. — Melting points are uncorrected. Optical rotations were measured with a Zeiss Kreispolarimeter. N.m.r. spectra were recorded on a JEOL FX-100 Fourier-transform spectrometer operating at 100 MHz for ^{1}H and at 25 MHz for ^{13}C. Chemical shift values are relative to internal tetramethylsilane, and accurate to

~0.05 p.p.m. for ^{13}C and ~0.01 p.p.m. for ^{1}H resonances. The H,H coupling constants were derived directly from multiplet spacings, and are accurate, in most cases, to ~0.2 Hz. ^{1}H-Signals were assigned using double-irradiation techniques.

T.l.c. was performed on silica gel GF (Merck), with detection by u.v. fluorescence, or by spraying with 10% ethanolic sulfuric acid and heating. Preparative t.l.c was performed on silica gel PF_{254} (Merck), and column chromatography on a column (65 × 2 cm) containing a mixture of silica gel H (65 g) and Celite (40 g) (Kemika, Zagreb, Yugoslavia). Dichloromethane–diethyl ether (10:1.5) was used as the solvent for chromatographic separations, except when stated otherwise.

3-Phenylpropan-1-ol was prepared by $LiAlH_4$ reduction of cinnamic acid in tetrahydrofuran[17] and purified by preparative t.l.c. Other alcohols were obtained from commercial sources, and were dried before use. 2,3,4-Tri-*O*-acetyl-β-L-arabinopyranosyl bromide (**1**), m.p. 134–139 °, $[\alpha]_D$ +284 (*c* 1.15, chloroform), was prepared after Barczai-Martos and Körösy[18].

2,3,4-Tri-O-acetyl-L-arabinopyranose (**22**). — To a solution of **1** (474 mg, 1.4 mmol) in absolute acetone (10 mL), stirred in an ice-bath, were added water (16.1 μL, 0.84 mmol) and aliquots of silver carbonate (325 mg, 1.18 mmol) as described for the preparation of 2,3,4,6-tetra-*O*-acetyl-D-glucopyranose[19]. The product was eluted from a column of silica gel with dichloromethane–ether (2:1, 150 mL; and 1:1, 400 mL), to yield semi-crystalline **22αβ** (384 mg, 99%). R_f 0.40 (2:1 dichloromethane–ether). ^{13}C-N.m.r. data ($CDCl_3$): δ 170.54, 170.22 (acetyl $CO\alpha\beta$); 20.91, 20.80, 20.70, 20.61 (acetyl $CH_3\alpha\beta$); 95.92 (C-1α); 71.09, 70.32, 68.13 (C-2,3,4α); 64.05 (C-5α); 90.74 (C-1β); 69.21, 68.79, 67.01 (C-2,3,4β), and 60.17 (C-5β). Signal intensities obtained with inverse, gated proton decoupling indicated an αβ-ratio of 3:7. ^{1}H-N.m.r. data (C_6D_6): δ 1.71, 1.70 (2 s, 2 OAcα); 1.74 (s, OAcαβ); 1.69, 1.66 (2 s, 2 OAcβ); 3.02 (bs, vanishing on addition of D_2O, OH); 4.37 (d, $J_{1,2}$ 7.3 Hz, H-1α); 5.41 (dd, $J_{2,3}$ 9.9 Hz, H-2α); 5.08 (dd, $J_{3,4}$ 3.5 Hz, H-3α); 5.24 (ddd, H-4α); 3.66 (dd, $J_{4,5a}$ 2.4 Hz, H-5aα); 2.91 (dd, $J_{4,5b}$ 1.4 Hz, $J_{5a,5b}$ 13.3 Hz, H-5bα); 5.46 (d, $J_{1,2}$ 3.5 Hz, H-1β); 5.48 (dd, $J_{2,3}$ 11.9 Hz, H-2β); 5.73 (m, $J_{3,4}$ 3.4 Hz, H-3β); 5.43 (hidden m, H-4β); 3.86 (dd, $J_{4,5a}$ 1.1 Hz, H-5αβ); and 3.43 (dd, $J_{4,5b}$ 2.1, $J_{5a,5b}$ 13.0 Hz, H-5bβ).

Anal. Calc. for $C_{11}H_{16}O_8$: C, 47.83; H, 5.84. Found: C, 47.83; H, 5.72.

Condensation of **1** *with alcohols.* — Reactions were carried out in the dark, at room temperature, in anhydrous dichloromethane–ether (3:1). To a stirred solution of the alcohol (1.3 mmol) in solvent (20 mL) containing anhydrous calcium sulfate (0.5 g) and dry silver oxide (0.15 g, 0.65 mmol) was added, in small portions during 1 h, a solution of **1** (1.1 mmol) in the same amount of solvent. Monitoring of the reaction by t.l.c. showed almost instantaneous consumption of **1** and a constant product ratio throughout. The mixture was further agitated, during storage overnight, to avoid decomposition, and was then centrifuged. The supernatant solution was concentrated *in vacuo*, and the residue was immediately subjected to column chromatography. The peracetylated orthoesters (**12**–**21**), with the initial fractions enriched in the *endo* isomers, were eluted before the corresponding arabinoside tri-

acetates (**2–11**). For the isolation of by-products, the ether content of the eluent was gradually increased to 50%. Final purification of syrupy compounds was achieved by re-chromatography on the same column, or, with u.v.-absorbing aglycons, by preparative t.l.c. Crystalline glycosides were recrystallised from 50–70% aqueous ethanol.

(*a*) *2-Phenylethanol.* The quantities of calcium sulfate and silver oxide, and, if not stated otherwise, the overall solvent volume were kept unchanged, and the product was isolated by preparative t.l.c.

2-Phenylethanol and **1** were condensed in various solvent mixtures detailed in Fig. 1 and Table I, which also contain overall yields and the resulting **14**:**4** ratios.

A solution of **1** (388 mg, 1.14 mmol) in dichloromethane (15 mL) was added to a solution of 2-phenylethanol (161 mg, 1.32 mmol) in ether (20 mL), to give **4** (186 mg, 45%), **14** (26 mg, 6%), and **22** (95 mg, 30%).

When an excess of 2-phenylethanol (1.56 g, 12.78 mmol) was condensed with 1.18 mmol (0.40 g) of **1**, column chromatography of the products gave **4** (366 mg, 82%) and **14** (20 mg, 4%).

(*b*) p-*Nitrophenylmethanol and 3-phenylpropan-1-ol.* Under the general conditions, *p*-nitrophenylmethanol gave a **13**:**3** ratio of 1:1.4 and an overall yield of 38%, whereas the respective values were 1:7.2 and 39% in dichloromethane–ether (85:15). A 1:1 mixture of these solvents afforded **3** (29%) and negligible amounts of **13**.

For 3-phenylpropan-1-ol, the dichloromethane–ether proportions, the resulting **15**:**5** ratios, and the overall yields were: 75:25, 1:2.0, 62%; 85:15, 1:3.7, 55%; and 50:50, 1:2.7, 59%.

2,3,4-Tri-O-*acetyl*-L-*arabinopyranose* (**22αβ**). — Compounds **1** (401 mg, 1.18 mmol) and **22αβ** (414 mg, 1.5 mmol) were treated by the general method; the product mixture was subjected to column chromatography [elution with dichloromethane–ether, 3:1 (400 mL) and 1:1 (500 mL)] to give minor amounts of unknowns, recovered **22** (337 mg, 46%), and the following products.

3,4-Di-*O*-acetyl-1,2-*O*-[1-*exo*-(2′,3′,4′-tri-*O*-acetyl-α-L-arabinopyranosyloxy)-ethylidene]-β-L-arabinopyranose (**24**; 125 mg, 19%), $[\alpha]_D$ +56° (*c* 1.9, chloroform), R_F 0.57 (2:1 dichloromethane–ether). ^{13}C-N.m.r. data ($CDCl_3$): δ 170.19, 169.99, 169.77, 169.04 (5 acetyl CO); 20.88, 20.73, 20.61 (5 acetyl CH_3); 121.36 (ethylidene C-1); 23.90 (ethylidene C-2); 97.30 (C-1); 74.56, 69.00, 65.88 (C-2,3,4); 62.36 (C-5); 94.52 (C-1′); 70.16, 68.60, 67.48 (C-2′,3′,4′); and 63.26 (C-5′). ^{1}H-N.m.r. data (C_6D_6) δ 1.71, 1.68, 1.66, 1.60, 1.58 (in $CDCl_3$: 2.14, 2.12, 2.08, 2.07, 2.03; 5 s, 15 H, 5 OAc); 1.74 (in $CDCl_3$: 1.70; s, 3 H, ethylidene CH_3); 5.70 (in $CDCl_3$: 5.59; d, 1 H, $J_{1,2}$ 4.6 Hz, H-1); 4.47 (dd, 1 H, $J_{2,3}$ 5.6 Hz, H-2); 5.43 (dd, 1 H, $J_{3,4}$ 3.7 Hz, H-3); 5.31 (q, 1 H, H-4); 3.74 (dd, 1 H, $J_{4,5a}$ 3.8 Hz, H-5a); 3.48 (dd, 1 H, $J_{4,5b}$ 3.8, $J_{5a,5b}$ 12.6 Hz, H-5b); 4.71 (d, 1 H, $J_{1',2'}$ 7.0 Hz, H-1′); 5.56 (dd, 1 H, $J_{2',3'}$ 8.7 Hz, H-2′); 5.10 (dd, 1 H, $J_{3',4'}$ 3.5 Hz, H-3′); 5.21 (m, 1 H, H-4′); 3.66 (in $CDCl_3$: 4.05; dd, 1 H, $J_{4',5a'}$ 3.2 Hz, H-5a′); and 2.92 (in $CDCl_3$: 3.64; dd, 1 H, $J_{4',5b'}$ 1.7, $J_{5a',5b'}$ 12.9 Hz, H-5b′).

Anal.: Calc. for $C_{22}H_{30}O_{15}$: C, 49.44; H, 5.66. Found: C, 49.49; H, 5.90.

3,4-Di-*O*-acetyl-1,2-*O*-[1-*exo*-(2′,3′,4′-tri-*O*-acetyl-β-L-arabinopyranosyloxy)-ethylidene]-β-L-arabinopyranose (**25**; 57 mg, 9%), $[\alpha]_D$ +117° (*c* 4.3, chloroform), R_F 0.61 (2:1 dichloromethane–ether). ^{13}C-N.m.r. data ($CDCl_3$): δ 170.18, 169.97, 169.69, 169.60 (5 acetyl CO); 20.91, 20.73 (5 acetyl CH_3); 122.41 (ethylidene C-1); 24.53 (ethylidene C-2); 97.29 (C-1); 75.08, 68.88, 65.81 (C-2,3,4); 62.37 (C-5); 90.54 (C-1′); 68.46, 67.76, 66.98 (C-2′,3′,4′); and 61.15 (C-5′). ^{1}H-N.m.r. data (C_6D_6): δ 1.75, 1.69, 1.62, 1.57 (in $CDCl_3$: 2.11, 2.11, 2.07, 2.01; 4 s, 15 H, 5 OAc); 1.77 (in $CDCl_3$: 1.72; s, 3 H, ethylidene CH_3); 5.46 (in $CDCl_3$: 5.56; d, 1 H, $J_{1,2}$ 3.9 Hz, H-1); 4.37 (dd, 1 H, $J_{2,3}$ 5.2 Hz, H-2); 5.46 (dd, 1 H, $J_{3,4}$ 3.4 Hz, H-3); 5.28 (td, 1 H, H-4); 3.67 (dd, 1 H, $J_{4,5a}$ 4.7 Hz, H-5a); 3.40 (dd, 1 H, $J_{4,5b}$ 4.7, $J_{5a,5b}$ 12.4 Hz, H-5b); 5.8–5.6 (m, 3 H, H-1′,2′,3′), 5.4–5.5 (hidden m, H-4′); 3.75 (in $CDCl_3$: 4.14; dd, 1 H, $J_{4',5a'}$ 1.2 Hz, H-5a′); and 3.33 (in $CDCl_3$: 3.70, dd, 1 H, $J_{4',5b'}$ 1.9, $J_{5a',5b'}$ 13.1 Hz, H-5b′).

Anal.: Calc. for $C_{22}H_{30}O_{15}$: C, 49.44; H, 5.66. Found: C, 49.71; H, 5.38.

Compound **26**, tentatively identified as 2,3,4-tri-*O*-acetyl-α-L-arabinopyranosyl 2,3,4-tri-*O*-acetyl-α-L-arabinopyranoside (20 mg, 3%), R_f 0.53 (2:1 dichloromethane–ether). ^{13}C-N.m.r. data ($CDCl_3$): δ 170.06, 168.99 (acetyl CO); 20.84, 20.66, 20.56 (acetyl CH_3); 95.12 (2 C-1); 68.95, 68.80, 66.37 (2 C-2,3,4); and 61.06 (2 C-5). ^{1}H-N.m.r. data (C_6D_6): δ 4.88 (d, 2 H, $J_{1,2}$ 5.5 Hz, 2 H-1); 5.54 (dd, 2 H, $J_{2,3}$ 7.1 Hz, 2 H-2); 5.25 (dd, 2 H, $J_{3,4}$ 3.2 Hz, 2 H-3); ~5.3 (hidden m, 2 H, 2 H-4); 3.76 (dd, 2 H, $J_{4,5a}$ 4.8 Hz, 2 H-5a); 3.08 (dd, 2 H, $J_{4,5b}$ 2.6, $J_{5a,5b}$ 12.2 Hz, 2 H-5b); and 1.79, 1.65, 1.60 (3 s, 18 H, 6 OAc).

Silver oxide-catalysed decomposition of **1**. — A solution of **1** (392 mg, 1.16 mmol) in dichloromethane–ether (3:1, 20 mL) was added to a suspension of silver oxide (150 mg, 0.65 mmol) and anhydrous calcium sulfate (0.5 g) in the same solvent, as specified in the general procedure. Column chromatography of the product mixture [elution with dichloromethane–ether, 10:1.5 (150 mL), 3:1 (80 mL), 2:1 (150 mL), and 1:1 (400 mL)] gave **22** (171 mg, 53%), **23** (16 mg, 3%), and **24** (41 mg, 7%), and minor amounts of unknown compounds.

Characterisation of products. — Analytical data, m.p., and specific rotations of compounds **2**–**21** are summarised in Table III. N.m.r. data are presented in Tables IV and V. While the ^{13}C spectrum of **6** accords with published values[20], variation of the aglycon moiety causes shielding of C-1 by up to 6 p.p.m., which is more than the chemical shift difference reported[20] for **6α** and **6β**. Orthoesters **12**–**21** showed singlets (2C) in the acetyl carbonyl and methyl regions, the ethylidene C-1,2 at ~123 and ~24 p.p.m., respectively[21], and the anomeric C shifted to ~97 p.p.m. Also, their H-2 resonances were ~1 p.p.m. below those of the corresponding arabinosides, and the ethylidene CH_3 signal was separated from the acetyl signals. Vicinal H,H-coupling constants are of the same order of magnitude as those described for β-L-arabinopyranose 1,2-(indol-1-yl orthoacetates)[30], α-D-glucopyranose 1,2-(alkyl orthoacetates)[19], 4,6-*O*-benzylidene-α-D-galactopyranose 1,2-orthoesters[22], and 1,2-*O*-alkylidene-aldopyranose derivatives[23,24], thus confirming the skew conformation of the pyranoid system caused by the presence of a 1,2-*cis*-fused dioxolane ring. The

exo-alkoxyl isomers of **12–21** were distinguished from their *endo* analogues by the reported[10,25] larger chemical shift of the signals for the ethylidene CH_3 protons.

Compounds **24** and **25**, established as isomers by elemental analysis, showed the ^{13}C signals of *arabino*-orthoesters (Table IV) and additional sets of peaks at chemical shifts close to those observed for **22α** (for **24**) and **22β** (for **25**). Similar analogies hold for the ^1H-n.m.r. spectra. Also, the specific rotation is more positive for **25**.

Compound **26** was available in relatively small and impure samples, and the n.m.r. assignment of structure is therefore tentative. The number of ^{13}C and ^1H signals was the same as for **22**, except that there was no evidence for the existence of free hydroxyl group (proton spectrum unchanged on addition of D_2O). These data are consistent with a symmetrical dimer, while the synthetic route used and the C-1,1′ shifts suggest the 1,1′-linkage. The α,α-configuration is indicated by the H,H-coupling constants and the large, benzene-induced difference in chemical shift for H-5a and H-5b, which was also observed for some α-L-arabinopyranoside triacetates (Table V), **22α**, and the 2,3,4-tri-*O*-acetyl-α-L-arabinopyranosyl moiety of **24**, whereas this difference was smaller for **22β** and the acetylated β-L-arabinopyranosyl moiety of **25**.

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REFERENCES

1 K. IGARASHI, *Adv. Carbohydr. Chem. Biochem.*, 34 (1977) 243–283.
2 B. HELFERICH AND K. WEIS, *Chem. Ber.*, 89 (1956) 314–321.
3 A. J. KHORLIN, A. F. BOCHKOV, AND N. K. KOCHETKOV, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1964) 2214–2216.
4 G. WULFF, G. RÖHLE, AND W. KRÜGER, *Chem. Ber.*, 105 (1972) 1097–1110.
5 G. WULFF, G. RÖHLE, AND U. SCHMIDT, *Chem. Ber.*, 105 (1972) 1111–1121.
6 G. WULFF AND G. RÖHLE, *Chem. Ber.*, 105 (1972) 1122–1132.
7 G. WULFF AND W. SCHMIDT, *Carbohydr. Res.*, 53 (1977) 33–46.
8 J. TIMMERMANS, *The Physico-Chemical Constants of Binary Systems in Concentrated Solutions*, Vol. 1, Interscience, New York, 1959.
9 B. B. HOWARD, C. F. JUMPER, AND M. T. EMERSON, *J. Mol. Spectrosc.*, 10 (1963) 117–130.
10 R. U. LEMIEUX AND A. R. MORGAN, *Can. J. Chem.*, 43 (1965) 2199–2204.
11 N. K. KOCHETKOV, A. F. BOCHKOV, T. A. SOKOLOVSKAYA, AND V. J. SNYATKOVA, *Carbohydr. Res.*, 16 (1971) 17–27.
12 B. CAPON, *Chem. Rev.*, 69 (1969) 407–498.
13 H. S. ISBELL AND H. L. FRUSH, *J. Res. Natl. Bur. Stand.*, 43 (1949) 161–171.
14 J. LEHMANN, *Chemie der Kohlenhydrate*, Georg Thieme Verlag, Stuttgart, 1976, p. 105.
15 H. R. GOLDSCHMID AND A. S. PERLIN, *Can. J. Chem.*, 39 (1961) 2025–2035.
16 P. J. GAREGG AND I. KVARNSTRÖM, *Acta Chem. Scand., Ser. B*, 30 (1976) 655–658.
17 R. F. NYSTRÖM AND W. G. BROWN, *J. Am. Chem. Soc.*, 69 (1947) 2548–2549.
18 M. BARCZAI-MARTOS AND P. KÖRÖSY, *Nature (London)*, 165 (1950) 369.
19 C. M. MCCLOSKEY AND G. H. COLEMAN, *Org. Synth., Coll. Vol.*, 3 (1955) 434–436.
20 A. I. KALINOVSKII AND E. V. EVTUSHENKO, *Khim. Prir. Soedin.*, (1979) 6–8.

21 H. KUNZ AND A. HARREUS, *Justus Liebigs Ann. Chem.*, (1982) 41–48.
22 A. F. BOCHKOV, V. M. DASHUNIN, AND N. K. KOCHETKOV, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1975) 632–638.
23 B. COXON AND L. D. HALL, *Tetrahedron*, 20 (1964) 1685–1694.
24 C. CONE AND L. HOUGH, *Carbohydr. Res.*, 1 (1965) 1–9.
25 A. S. PERLIN, *Can. J. Chem.*, 41 (1963) 399–406.
26 C. E. BALLOU, S. ROSEMAN, AND K. P. LINK, *J. Am. Chem. Soc.*, 73 (1951) 1140–1144.
27 P. L. DURETTE AND D. HORTON, *Carbohydr. Res.*, 18 (1971) 403–418.
28 N. K. KOCHETKOV, A. J. KHORLIN, AND A. F. BOCHKOV, *Tetrahedron*, 23 (1967) 693–707.
29 B. LINDBERG, *Acta Chem. Scand.*, 6 (1952) 949–952.
30 T. N. SOKOLOVA, V. E. SHEVCHENKO, AND M. N. PREOBRAZHENSKAYA, *Carbohydr. Res.*, 83 (1980) 249–261.